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The Metallurgist.

Supplement to **The Engineer**, *December, 1936.*

Copper-Nickel Alloy Tubes.

SEVERAL non-ferrous alloys of the copper-rich type have been, and are being, used for condenser tubes. The conditions of service in this application are complicated and may vary very considerably from one installation to another, in many respects other than that of the composition of the cooling water, which, although very important, is but one of the several factors affecting the life of the tubing. The suitability of different alloys for condenser tubes is a subject which has received a good deal of attention in the past, and in view of its importance this is not surprising; nor is it surprising, when the variation in severity of service conditions is considered, that quite a number of alloys continue to be used.

With the development of turbine-driven ships involving greater velocities of the cooling water in the condensers, the need arose for a more serviceable material than Admiralty brass and other alloys which had hitherto been employed. Alloys of the cupro-nickel type were first used commercially in the form of condenser tubes in a land installation some fourteen years ago, and since that time the use of these alloys in this application has very considerably extended. As might be expected, it is in the condensers of naval vessels and large ocean liners that the use of cupro-nickel has become more general, for it is in such installations with their exacting service conditions that the merits of the alloys are most likely to manifest themselves. The properties of these alloys are quite well known, and there have been enough corrosion experiments made and enough service experience accumulated to demonstrate the suitability of cupro-nickel for tubes under conditions of sea water service. In the earlier days of their development the 80 per cent. copper and 20 per cent. nickel alloy was commonly employed, but the 70/30 alloy later began to be used to an increasing extent, and since 1931 it is the composition which has been supplied to British Admiralty requirements.

Following tests initiated in 1925, the U.S. Navy became interested in copper-nickel alloys for condenser tubes, and the 70/30 alloy forms the subject of a paper by M. S. Noyes in the February issue of the *Journal* of the American Society of Naval Engineers, in which its properties are reviewed, and the reasons given why the Bureau of Engineering selected it from all the alloys possessing reasonable corrosion resistance to sea water conditions for salt water piping. At the Naval Engineering Experiment Station, corrosion tests involving (*a*) rapid rotation while semi-submerged in brackish water, (*b*) slow movement through a circular path in an electrolytic cell containing brackish water, and (*c*) close exposure to an impinging jet of brackish water carrying entrained air were carried out. Several alloys were included in the tests, and the most satisfactory results were in general obtained with cupro-nickel alloys. The tests made on joints with standard fittings showed that when the joints were effected either with a 50 per cent. lead-tin solder or a silver solder, no marked corrosion could be detected. Further information regarding the corrosion resistance of copper-nickel alloys to marine conditions is given by reference to tests carried out at three stations along the Atlantic coast in connection with which specimens were examined for loss in weight, pitting on the surface, concentrated electrolytic cell effects at the specimen supports, corrosion attack at the sheared edges and fouling, and also by reference to the work of Friend, of Worthington, and of Bauer. Examples of installations are also quoted to show the satisfactory service which has been obtained with tubes of these alloys.

J. A. Duma, in a paper in the August issue of the same *Journal*, deals with the metallurgical properties of the 70/30 alloy, and more particularly with the cause of failure of some tubes on rolling and belling into the plates. Of six such tubes studied, five failed to withstand cracking after a 50 per cent. increase in internal diameter in the drift-pin expansion test, none of them stood up to the expanding and belling test, and in a flattening test they showed various degrees of cracking. The results of these tests are not surprising in view of the failure of the tubes on expanding into the plates. The tensile test results on only two of the six tubes are given, and one shows a tensile strength of almost twice that of the other. The microstructure of this particular sample suggests that it has been ineffectively annealed or not annealed at all. The recommended annealing treatment is to quench in water from about 870 deg. Cent. The presence of excess oxide in some of the tubes was established by microscopic examination and by corrosion tests in a mercurous nitrate solution. It is stated that a high percentage of embrittling copper oxide in the alloy will result in tubes splitting on expanding, and although photomicrographs are shown no actual chemical figures for oxide contents are included. Since tubes containing oxide inclusions, even when thoroughly annealed, will not pass either the drift-pin expansion or the belling test, the importance of adequate deoxidation is apparent. It is also affirmed that when the copper content exceeds 80 per cent. the tubes will not pass these tests even when completely annealed.

In connection with the heat treatment experiments which were made, hardness values are given for one alloy, samples of which, after quenching from 900 deg. Cent., were heated for six hours at various temperatures ranging up to 650 deg. Cent. The results which show a maximum increase on reheating of more than

40 Brinell numbers suggest that the alloy is age-hardenable to an appreciable extent. The analysis given indicates that 0·14 per cent. of manganese was the only element present other than copper and nickel. From work carried out by English investigators, it is known that comparatively small amounts of such elements as aluminium and silicon, for example, in cupro-nickel, render the alloy age-hardenable, but the absence of these elements and of such others as tin and phosphorus leaves the cause of the observed hardening effect a very open question, especially since some of the materials examined showed it, whereas others did not.

Pre-Precipitation Hardening.

IT has been known for several years that in certain age-hardenable alloys precipitation of finely divided particles occurs simultaneously with the changes in hardness, while in other alloys these changes take place prior to or without any precipitation. The silver-copper alloys are generally considered to be a typical example of the first group, while the "duralumin" alloys are typical of the second group. The two types of ageing have been discussed in detail by P. D. Merica,[1] who, in a review of "The Age Hardening of Metals," put forward the explanations known as the precipitation theory and the knot theory respectively. The latter theory attributes hardening to the migration of atoms of the solute in the supersaturated solid solution to form groups, clusters, or "knots." The irregular lattice distortion so produced has an influence on the resistance to deformation, or hardness.

The solute atoms ultimately occupy positions which must approximate closely to those which they will have in the crystallite that is to be precipitated. It is well recognised now that these theories do not conflict with each other, the one used for a given ageing system depends on which way the alloy in question happens to age harden.

Dr. M. L. V. Gayler and Mr. G. D. Preston[2] have also put forward a theory of age hardening based on the idea that the decomposition of the solid solution takes place in two stages, the first being the rejection of atoms of the dissolved metals from the lattice of the solid solution, accompanied by the possible formation of molecules, and the second consisting of a coagulation of these rejected atoms and molecules to form small groups of crystallites. In their opinion the latter process probably starts just after the first and rapidly overtakes it until the lattice strain which is caused by the first stage is diminished and finally removed by the complete precipitation of the dissolved atoms or molecules.

Pre-precipitation rearrangement has been discussed by Professor John T. Norton[3] in connection with copper-iron alloys. In the present article the term "knot" is used for the pre-precipitation stage in conformity with the practice of the author whose work is to be reviewed,[4] but without implying endorsement of any particular view of the mechanism of the changes occurring at this stage.

Work on the aluminium-copper (duralumin) alloys, in which precipitation does not occur during ageing at atmospheric temperature, has shown that if the ageing temperature is raised sufficiently hardening will be accompanied by actual precipitation. Hardening of the quenched alloy at room temperature is not brought about by the same process as accelerated ageing by precipitation at 150 deg. to 200 deg. Cent. In fact, it is quite probable that all of the so-called knot-hardening alloys will harden by precipitation at elevated temperatures. Therefore, a combination of knot and precipitation theories is necessary to give a complete picture of the age hardening of these alloys, and it appears that knot formation and precipitation are not independent processes. To test the validity of this idea, it is necessary to ascertain whether alloys that commonly harden by precipitation will harden before precipitation begins if the ageing temperature is sufficiently lowered.

With this object in view, the ageing characteristics of the silver-copper alloys have been carefully re-examined by Morris Cohen[4] at ageing temperatures somewhat below those mainly used by previous investigators. He has detected hardening and accompanying effects on other physical properties in these alloys before any precipitation has taken place, and so given added support to the idea that knot formation must precede precipitation, and that they form two consecutive steps in the general mechanism of age hardening.

The silver-rich end of the silver-copper diagram is shown in Fig. 1. The alloy used by Mr. Cohen

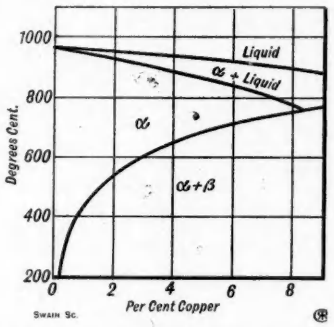


FIG. 1—*Solid Solubility of Copper in Silver.*

in his experiments contained 8·72 per cent. of copper, and was thus just within the maximum solubility limit of copper in silver (8·8 per cent.) at 779·4 deg. Cent. The solubility decreases to 0·1 per cent. at atmospheric temperature, and ageing was studied after treatment at 25 deg. intervals between 100 deg. and 200 deg. Cent. inclusive. The 8·72 per cent. copper-silver alloy, prepared from very pure metals, was chill cast, cold rolled to a 50 per cent. reduction in area, and annealed in nitrogen at 750 deg. Cent. for 160 hours. It was then cut up into suitable specimens for hardness tests, X-ray and microscopic examination, dilatometric measurements, and wire drawing to provide for conductivity tests. The solution treatment given to all specimens was carried out in a purified nitrogen atmosphere and consisted

[1] "Trans.," A.I.M.E., 1932, 99, 13.

[2] *Journ.*, Inst. Met., 1929, No. 1, 41, 191.

[3] "Metals Technology," December, 1934, A.I.M.E. Tech. Pub., 586.

[4] Morris Cohen, "Ageing Phenomena in a Silver-rich Copper Alloy," "Metals Technology," October, 1936, A.I.M.E. Tech. Pub, 751.

of heating for two hours at 765 ± 2 deg. Cent., followed by water quenching.

The hardness tests carried out after ageing give results of great interest which are shown in Fig. 2, the abscissæ, representing time, being plotted on a logarithmic scale. The curves indicate a definite incubation period at all temperatures. At 100 deg. Cent. the hardness rises to a low maximum with subsequent softening. This, however, is not due to "over-ageing," because later it again increases to a far higher value. This primary peak is clearly shown after treatment at 100 deg. and 125 deg. Cent., less clearly at 150 deg., and not at all at 175 deg. and

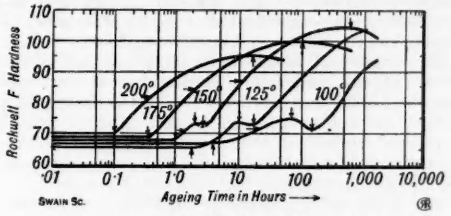


FIG. 2—*Changes in Hardness During Ageing.*

200 deg. for which temperatures the ageing curves show the usual single hardness maximum.

X-ray data show a gradual displacement of the diffraction lines of the super-saturated solid solution, indicating that the initial precipitation is progressive, not proceeding to completion at any point. There is no visible change in the microstructure during this stage. After a time, new lines, characteristic of the solid solution saturated with copper at the particular ageing temperature, appear and become more and more intense while the original lines continue to shift, become fainter and finally disappear. During this stage the microstructure shows precipitation in the form of darkened areas at the grain boundaries and on the twinning planes. These areas grow until the precipitation is complete. A comparison of the times which elapse before the beginning of hardening and the beginning of precipitation is given in the table :—

Comparison of Beginning of Hardening and of Precipitation.

Ageing temperature.	Beginning of hardening.	Beginning of precipitation.
100 deg. Cent.	4 hr.	70–140 hr.
125 „ „	2 hr.	10–16 hr.
150 „ „	1 hr.	2–3 hr.
175 „ „	27 min.	15–30 min.
200 „ „	6 min.	6–8 min.

Electrical resistivity first increases in the initial stage and then decreases as precipitation proceeds. Dilatometric measurements show similar changes, the normal contraction which accompanies precipitation being preceded by a slight expansion. These effects occur even at 200 deg. Cent. though the initial stage is not revealed by hardness tests, showing that the mechanism of ageing (but not of hardening) is the same at all temperatures, viz., knot formation followed by precipitation.

Examination of all the data led Mr. Cohen to the conclusion that, for the particular alloy containing 8·72 per cent. of copper, 169 deg. Cent. is the critical ageing temperature below which the beginning of hardening (as measured by the Rockwell F. scale) occurs simultaneously with precipitation. Below 169 deg. Cent. double hardness peaks occur in the ageing curves, the first being due to knot formation, the intermediate softening to the relief of strain when precipitation takes place, and the second peak to the attainment, by the precipitated particles, of the critical size and distribution necessary for maximum hardening. Above 169 deg. Cent. the hardness curves consist of the usual single peak, the entire hardening being due to precipitation. The mode of precipitation is the same at all temperatures. The initial precipitation is gradual, but becomes more and more non-uniform as precipitation goes rapidly to completion in localised regions at the grain boundaries and twinning planes. These regions grow at the expense of the progressively precipitating areas until the precipitation process is complete.

The fundamental mechanism of ageing of the silver-copper alloys therefore appears to be quite similar to that of the aluminium-copper alloys of the duralumin type in that both will harden by a pre-precipitation or by a precipitation process according to the conditions of ageing. The detection of these pre-precipitation effects in the silver-copper alloys is sufficient to indicate that any classification of age-hardenable systems into knot-hardening and precipitation-hardening groups is both arbitrary and unnecessary.

Fissures in Railroad Rails.

A SECOND Progress Report of the Joint Investigation of Fissures in Railroad Rails, conducted by the Engineering Experiment Station, University of Illinois, in co-operation with the Association of American Railroads and the Rail Manufacturers' Technical Committee,* has now been published.

The Report, while confirming the results published in the first Progress Report, does not add very much further light on the question of what are the chief cause or causes of shatter cracks in rails. It is again emphasised that these shatter cracks are, with very little doubt, the genesis of all transverse fissure failures.

It is remarked that in a Press review of the first Report it was pointed out that sufficient emphasis had not been placed on chemical and metallographic work, which might have definitely settled the cause of production of shatter cracks, but it is explained that such investigations have not led to any definite results, and it is very uncertain whether any one cause can explain the phenomenon.

The further study of the prevention of shatter cracks in rails at the mill, either by controlled cooling or normalising, has, however, confirmed the results given in the first Report that no internal fissures have been developed in such rails under the laboratory rolling load test machine.

The controlled cooling processes are described as in "commercial" use in Canada and in an "experimental" way in America. As, however, three of the leading rail manufacturers in America are now operating a controlled cooled process under the Sandberg patents and up to date have supplied over 250,000 tons to various railways, the expression "experimental" would appear to be somewhat misleading.

Further sections of the Report are as follows :—

Microphone Test for Cracking of Rails while Cooling.—Attempts were made to determine the

* Published by the University of Illinois, Urbana, Illinois, U.S.A. Pages 26. Price 15c.

range of temperature during which shatter cracks form by attaching a microphone to a rail cooling from the mill and amplifying the microphone current so that records of the sounds could be obtained on a tape recorder. It was found, however, that sounds from the mill and those from the grating of the rail on its supports rendered the record useless, and a second test was made in which a simultaneous record was also made from a " dummy " cold rail laid alongside the cooling rail, and both supported from overhead with damping pads in the supports. The data from these tests are now being reduced and checked by etch tests from the rails, but no results are published.

In the reviewer's experience shatter cracking in susceptible heats occurs in short pieces (say, 6in. long) cut at the hot saw, with apparently the same frequency that it occurs on the full-length rails, and it would therefore appear to be easier to carry out these tests on such short lengths, which could be taken right away from the mill into a sound-proof laboratory, than to attempt to filter out mill noises which must greatly exceed any possible sound of the shattering.

Acceptance Tests for Rails are classified as destructive and non-destructive tests, but so far no test of the latter type has been evolved which will indicate the presence of shatter cracks in rails. Further research is proposed on this question and the possible use of " supersonic " waves suggested.

As regards destructive tests, which, it is recognised, can only be made on samples, the etch test gives positive results as to the presence or absence of shatter, but if used as an acceptance test might lead to controversy as to the importance of longitudinal shatter cracks or of transverse cracks deep in the rail. The relative value of the drop test and the autographic slow bend test are discussed, with decided preference for the latter as a detector of shatter. Sample autographic diagrams of the slow bend test on sound and shatter-cracked rails appear to show very marked differences.

Metallographic and Chemical Studies have led to no positive results which can be associated with shatter. While mention is made of current work on the importance of included gases, the evidence now available regarding hydrogen as a shatter forming factor is much stronger than the Report would suggest.

Tests of Rail Steel at Low Temperatures are being continued with the object of studying the effect of occasional heavy overloads on rail steel at temperatures down to 40 deg. Fah. below zero.

Tests of Batter of Rail at Joints.—The rolling load test machine is being used for these, and a diagram showing the deformation of a standard 130lb. rail joint after 5000, 104,000, 345,000, and 670,000 cycles is given.

Field Tests for Wheel Loads in Service have been continued and additional graphs are shown both for normal track and for a bridge track. While the percentage of heavy wheel loads is higher on the bridge track than on the ballasted track, it is pointed out that the bridge was selected merely as an example of stiff track, and the results do not necessarily indicate that transverse fissures would develop more rapidly in such locations, especially as the bending stresses on the rails would be less.

Discussing the data so far obtained, the view is expressed that at train speeds below 25 m.p.h. flat spots on wheels are a prominent cause of high wheel loads, at speeds between 40 and 50 m.p.h. hard spots in the track are prominent, while at speeds above 60 m.p.h. out-of-round wheels, unbalance in counterweights, and abnormally high track play are the important factors.

The calculations of wheel loads from the measurements of strain in the rail flange involve the assumption that a rail takes the same trend of elastic curve under slowly as under rapidly applied loads. Tests of a rail under impact bending loads have shown that under very rapid loading the inertia of the beam makes it act as if partially restrained at supports, and that therefore the load necessary to cause a given tensile stress is higher than would be indicated from the method used. It is, however, argued that the calculations are justified, as, though the actual wheel loads are probably higher than those reported, it is also fairly well established that steel is stronger under rapid than under slow applications of load.

Importance of Maintenance of Track and Rolling Stock.—Loads sufficient to spread shatter cracks into transverse fissures undoubtedly occur in ordinary service on well-maintained tracks. Apart from the improved methods of rail manufacture now employed, there must be, during the next ten years, thousands of shatter cracked rails in track, and the reduction of fissure failures must demand a high degree of co-operation between track and rolling stock engineers.

The reviewer would suggest that extensive use of the Sperry detector car would form the best safeguard for the elimination of such unsafe rails.

The bulletin concludes with a list of members on the Advisory Committee.

Iron-Cobalt-Copper Alloys.

ALTHOUGH the use of iron-cobalt-copper alloys has from time to time been advocated for special purposes, no account of the constitution of these alloys has appeared until quite recently. In the September number of *Archiv*, W. Jellinghaus* has published the results of a study of these alloys from which he concludes that there is complete solubility in the ternary liquid as in the corresponding binary systems. The alloys may be divided into three types when judged by their behaviour on solidification :

(1) In the iron corner of the diagram δ solid solution is first formed and afterwards transforms to γ.

(2) Alloys with a copper content up to 8 per cent. (with the exception of a small range of compositions in the iron corner) solidify as the γ solid solution.

(3) Alloys with a copper content of over 8 per cent., and up to 96 per cent. first deposit primary γ, and finally solidify as a mixture of γ and copper.

The liquidus and solidus temperatures were not studied in great detail, but the figures for a series of alloys containing 20 per cent. of copper are of interest. These results were as follows .—

	Per cent.					
Copper	20 per cent. in each alloy					
Cobalt	0	10	25	50	70	80
Iron	80	70	55	30	10	0
	Deg. Cent.					
Liquidus	1470	1440	1438	1427	1428	1440
Solidus	1094	1048	1071	1076	1084	1120

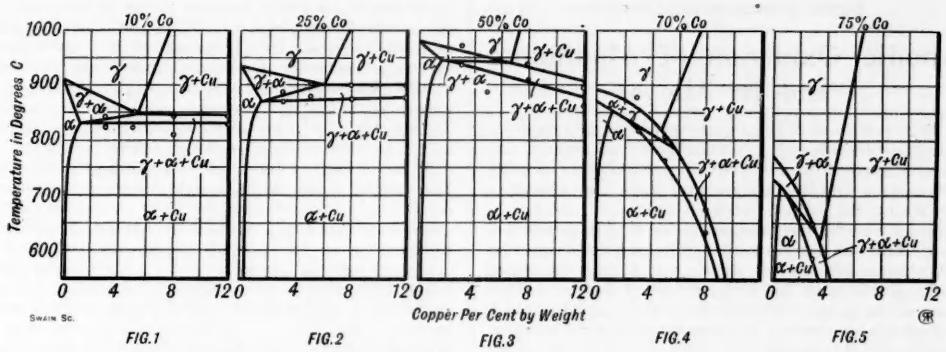
There is, therefore, at 20 per cent. of copper still

* *Archiv für das Eisenhüttenwesen*, 1936–37, 10, 115–118.

evidence of the minimum in the liquidus curve which characterises the iron-cobalt alloys.

Alloys with 12 per cent. of copper and cobalt contents of 10, 25, 50, and 70 per cent. showed clear indications of a thermal change at about 1100 deg. Cent., but alloys with similar cobalt content and 8 per cent. of copper no longer showed this point, which corresponds to the peritectic of the ternary copper-rich alloys. Thus, approximately 8 per cent. is the limit of solubility of copper in the γ solid solution, and this limit applies to the whole range of cobalt content. Below 1100 deg. Cent. the solubility of copper in γ was found to decrease. The extent of this diminution and also the temperatures of the γ-α transformation, determined dilatometrically, are shown in Figs. 1 to 5. The temperature of the transformation rises with increase in cobalt content to a maximum when the cobalt and iron occur in equal proportions, *i.e.*, on the section joining 50 : 50 from 800 deg. Cent. and then tempered at 550 deg. Cent., it was shown that precipitation hardening occurred in these alloys, and therefore that the copper content of the α solid solution falls with diminishing temperature. At room temperatures it would probably be under 1 per cent.

It has been widely maintained that the iron-cobalt system contains an ordered phase corresponding to the formula FeCo, and although the scope of the work of Jellinghaus did not permit of a thorough investigation of this subject, there were indications that this phase was present in the ternary system. The hardness of the alloy containing 50 per cent. of cobalt and 3 per cent. of copper quenched from below the change was higher than that of the 10, 25 or 70 per cent. cobalt alloys with the same copper content. The specific gravity of the alloys quenched from 1250 deg. Cent. was usually increased by annealing, but that of the alloy with 50 per cent. cobalt



FIGS. 1–5—*Sections with Constant Cobalt Content Across the Iron-Cobalt-Copper Diagram.*

cobalt-iron and 100 copper, and then falls again with higher cobalt contents, ultimately reaching room temperature.

All the alloys whose compositions lie between iron-copper, iron-cobalt, and the section joining 79 : 21 cobalt-iron and 100 copper showed the γ-α transformation; in those lying on the cobalt side of this section the transformation did not occur. Thus, the γ-α change was observed in alloys containing:

70 per cent. cobalt with 3, 5, and 8 per cent. copper.

75 per cent. cobalt with 3 per cent. copper;

but not in alloys containing:

70 per cent. cobalt with 12 per cent. copper.

75 per cent. cobalt with 8 per cent. copper.

80 per cent. cobalt with no copper.

These results were confirmed by means of hardness tests on quenched specimens.

The iron and cobalt content of the copper phase was not specially determined as it was regarded as sufficiently well known from the work of Tammann and Oelsen, who state that the maximum solubility of either iron or cobalt in copper is about 4 per cent. at the freezing point, and that it diminishes rapidly, so that a solubility of 0·5 per cent. is already reached at 600 deg. Cent. The solubility of copper in the α solid solution (in the binary system iron-copper, 1·3 per cent. according to Norton) was found in the ternary system to remain constant at about 1·5 per cent. up to 65 per cent. of cobalt and then to diminish. By hardness tests made on specimens quenched and 3 per cent. copper was, on the other hand, slightly diminished. The coefficient of thermal expansion of this alloy was relatively small. Its X-ray spectrum showed some lines not belonging to the α-iron lattice. These persisted after various treatments, but only when cobalt radiation was used and not with iron or chromium radiation. Thus, while the existence of FeCo in the ternary alloys of low copper content appeared to receive some confirmation, no actual identification of the ordered structure was obtained, and neither was any determination made of the limit of the hexagonal cobalt phase which, according to Masumoto, disappears at 5 per cent. of iron in the cobalt-iron system.

Further interest arises from the fact that almost simultaneously with the publication of this paper by Jellinghaus, studies of the iron-cobalt and the iron-cobalt-copper systems, carried out in the University of Sheffield, were described in the first report of the Alloy Steels Research Committee of the Iron and Steel Institute,† It is gratifying to note the generally satisfactory agreement of the conclusions in spite of the different aspects of the subject which engaged the attention of the English and German investigators.

Maddocks and Claussen agree with Jellinghaus in concluding that the alloys show complete miscibility in the liquid state, and that the solid solution, saturated with copper at the peritectic temperature, contains approximately 8 per cent. of copper

† Section VII, pp. 93–96 (J. H. Andrew and C. G. Nicholson); Section VIII, pp. 116–124 (W. R. Maddocks and G. E. Claussen).

irrespective of the iron-cobalt ratio. They agree with reference to the persistence of the minimum in the iron-cobalt liquidus in alloys of high copper content under 50 per cent. They both find the same rise in the temperature of the γ-α change with increase in cobalt to a maximum with about 50 per cent. cobalt and their actual temperatures for liquidus, solidus, and γ—α transformation show a good degree of consistency. The English investigators observed an unexpected arrest at about 727 deg. Cent. in the cooling curves of the 50 per cent. cobalt alloys with copper 0 to 10 per cent. This point does not appear in the German investigation. It is well below the γ-α change and may be connected with FeCo. The alloys of this composition are extremely brittle. The evidence for the existence of FeCo is slight in both investigations, but there is a sufficient hint of anomalous behaviour in the region corresponding to this composition to warrant further work.

Anodic Oxidation of Aluminium and Its Alloys.

THE resistance of most metals to corrosion depends to a considerable extent on the nature and continuity of the surface film. This is particularly so with aluminium and its alloys, and it is not therefore surprising that much research has been directed in recent years to the production of highly protective oxide films on these metals. The natural oxide film on aluminium has an average thickness of about $0{\cdot}2\,\mu$; this may be increased to 1–$2\,\mu$ by simple immersion of the metal in solutions of certain oxidizing agents, and to as much as $20\,\mu$ by anodic oxidation in suitable media.

In the anodic processes the aluminium hydroxide which is normally produced in the simple immersion processes is converted by the action of the current at the moment of its formation into a dehydrated, dense form which is intimately and firmly bound to the surface of the metal. This coating is of a peculiarly porous nature, such that, although the pores are of sub-microscopic dimensions, they allow the electrolyte to penetrate to the metal surface, so that the oxide layer grows inwards and the actual surface layer of the metal is converted in a hard, dense oxide film. The porosity of the film has other advantages, since it can be treated in various ways to increase its resistance to corrosion and to produce decorative effects.

The usual electrolytes employed in anodic oxidation consist of solutions of sulphuric, oxalic, or chromic acids or their salts, or of mixtures of two or more of these, the exact composition of the bath varying according to the desired hardness and porosity of the film. Since a relatively high current density is necessary owing to the resistance of the film, the bath tends to get hot, and an efficient cooling apparatus must therefore be provided, as films deposited from hot baths are unsatisfactory. Direct or alternating current may be used, although in the latter case oxidation occurs only when the metal is anodically polarised, but the periodic oscillations between anodic and cathodic polarisation produce favourable conditions for the formation of very dense films.

Anodic films may be applied to almost any of the commercial aluminium alloys, but the colour of the film varies with the nature of the alloying metals; with pure or ordinary commercial aluminium the film has the light, clear tone of pure alumina, whereas with alloys containing manganese, iron, silicon, or copper, it has a grey to dark bluish-grey colour. Satisfactory films cannot be produced on alloys with a high copper content in the usual baths, since the copper oxide produced by the oxidation goes into solution in the electrolyte, and the films become too porous. The previous heat treatment of the alloy has also an effect on the colour of the film produced, thus films on silicon alloys in which the silicon has been precipitated from solid solution by heat treatment are much darker than those on similar alloys in which it is retained in solid solution. In many cases the darkening effect of the alloying elements can be prevented by giving the metal a preliminary pickle in a bath which dissolves the alloying element from the surface layers.

Before placing the articles to be oxidised in the bath, they should be carefully degreased and all traces of foreign material removed from the surface. Care should be taken that no rolled-in inclusions of other metals are present, and, in the case of welded or riveted articles, that the weld metal or rivet metal has approximately the same dissolution potential as the remainder of the article, otherwise preferential severe oxidation and corrosion are likely to occur by the setting-up of local elements, with the result that severe pitting or even perforation may ensure.

When a film of the desired thickness is obtained the articles must be thoroughly washed to remove all traces of the electrolyte from the pores, which must then be closed to prevent ingress of corrosive material when the articles are in use. Closing of the pores may be effected in two ways, either by treatment with hot water or steam to make the film swell up by rehydration, and thereby produce automatic closure, or by filling the pores with inert organic materials, such as fats, waxes, or oils, or with a pigment which may be produced in the film by saturating it with a solution of a chemical, and then immersing the article in another solution which precipitates a coloured compound by interaction with the first solution. Barium sulphate, insoluble silicates or chromates, ferro-cyanides, metal oxides or hydroxides, and organic colouring matters have thus been produced directly in the pores of the film. If the film is to be used for insulation purposes in electrical apparatus, it must be carefully dried until all water is expelled and then impregnated with a suitable lacquer. Tests have shown that the insulating power of such impregnated films is greater than the sum of the insulating powers of the lacquer and the untreated film.

Another interesting property of anodic films is the fact that they may be dyed like a textile fabric, the alumina probably acting as a mordant for the dye; the whole of the film may be dyed a uniform colour, and useful or decorative designs in one or more colours may be applied by somewhat similar printing processes to those used in calico printing.

Recently the Siemens firm in Germany have found that the films may be used as photographic plates after impregnation with a light-sensitive silver or other salt. To prepare the surface the film is first impregnated with a soluble silver salt, then treated with a precipitant which deposits the light-sensitive silver compound in the pores. The sensitised film is then used as a photographic plate by the contact process, so that a positive image is produced on it; this image may be developed, fixed and toned by any of the ordinary methods. The resultant picture is extremely stable, and is quite unaffected by heating

up to temperatures at which the underlying aluminium melts.

In Germany anodically oxidised aluminium is known under the name of "Eloxal" and finds extensive use in the manufacture of scientific instruments, electrical apparatus, domestic utensils, and pistons, as well as for the construction of coachwork for road and railway vehicles, aircraft fuselages, window frames, shop fronts, wardrobes, and other articles of furniture, staircases, and innumerable small articles where lightness, resistance to corrosion, and a pleasant appearance are desired. Many examples of these uses are illustrated and discussed in recent articles by F. Nückel* and W. Birett† on "The Electrolytic Surface Treatment of Aluminium and its Alloys."

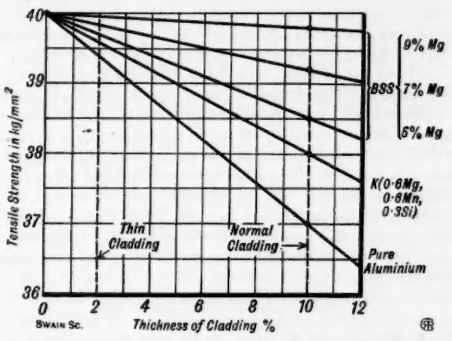
As mentioned above, the Eloxal films have a high electrical insulating power when the pores are completely sealed, and therefore cannot be coated with other metals by electro-deposition. The problem of plating aluminium with more resistant metals has engaged the attention of research workers for many years, but until relatively recently no satisfactory solution had been found. The difficulty has always been to remove the natural oxide film so as to obtain a clean surface for deposition of the protective metal. It has now been found that better adhesion of the deposit is obtained if, instead of removing this film, it is first thickened by the Eloxal process, and then rendered more porous by partial dissolution in a suitable solvent. After this treatment the plating metal can actually be deposited in the pores of the oxide film which anchor it firmly to the aluminium. When the thickness of the plating exceeds that of the oxide film a smooth bright uniform deposit over the whole article is obtained. This deposit is so firmly adherent and so ductile, in the case of nickel and chromium, that the plated metal may be twisted into spirals without causing flaking or cracking of the deposit. Unfortunately, no details of this method of plating are yet available (for patent reasons), but articles produced by the process have been subjected to severe tests by the State Testing Laboratory in Berlin-Dahlem, and the claims made for the behaviour of the plate are said to have been fully substantiated.

Clad Aluminium Alloys.

DESPITE the many improvements which have been made in the production of light, yet strong aluminium alloys since Wilm discovered duralumin in 1911, these alloys have suffered from the disadvantage that they are readily corroded, especially by salt water and in atmospheres containing salt spray. The reason for this behaviour is well known, namely, the presence of copper, magnesium silicide or other constituent which behaves as a cathode to pure aluminium. The only materials sufficiently resistant to corrosion by sea water known up to the present are pure aluminium and alloys of the hydronalium type, consisting of aluminium with various percentages of magnesium and small amounts of manganese. Very pure aluminium, produced by the Hoopes-Frary process or modifications of it, has an extraordinarily good resistance to salt water corrosion, but, of course, is much too soft to be used as a constructional material. Small additions of magnesium, manganese, and silicon improve the strength appreciably, while with 5 to 9 per cent. of magnesium and up to 1 per cent. of manganese a strong and highly resistant alloy is produced, which, however, is not amenable to age hardening, and is much inferior in strength to duralumin.

When the production of pure aluminium on the commercial scale became an accomplished fact, and its excellent resistance to corrosion was appreciated, attention was turned to the possibility of using it as a cladding material for duralumin and similar alloys. Experiments by the metallurgists of the Aluminum Company of America resulted in the successful commercial production of sheet duralumin clad on one or both sides with pure aluminium, and this duplex material was found to have the corrosion resistant properties of pure aluminium combined with the mechanical properties of duralumin. The material could be heat treated, fashioned in the soft state, and subsequently age hardened. With more prolonged experience of the material certain disadvantages began to show themselves; in the first place, for a definite thickness the tensile strength was always less than that of unclad duralumin, owing to the presence of the weaker outer layers, and, secondly, it was found that during heat treatment there was a tendency for the copper to diffuse from the core to the outside of the protective layer, thereby seriously reducing its resistance to corrosion, but at the same time increasing the strength of the cladding layer and therefore of the sheet.

During recent years numerous researches, especially in Germany, have been directed towards effecting improvements in the plating layer. These resulted in the development of Bondurplat, in which the cladding consists of an alloy of iron-free aluminium with magnesium 0·6, manganese 0·6, and silicon 0·3 per cent., and more recently of B.S.S. alloys, consisting of pure aluminium with 5, 7, or 9 per cent. magnesium and 0·6 to 1 per cent. manganese as cladding materials. The diagram shows the improvements effected in the



Influence of the Cladding Thickness on the Tensile Strength of Clad Duralumin Sheet.

tensile strength of duralumin, clad with these different alloys in various thicknesses.

From this it will be seen that with a 5 per cent. coating on each side pure aluminium reduces the tensile strength by 7·5 and the 9 per cent. magnesium alloy by only 2 per cent. The surface hardness of B.S.S.-clad material is about four times that of aluminium-clad material and the bending properties are about equal to those of the unclad duralumin. Again, the potential difference between the core and

* *Korrosion u. Metallschutz*, 1936, 12, 283.
† *Ibid.*, 290.

the cladding is with B.S.S. alloy about twice that with pure aluminium, so that the protective action of the former extends to a greater distance than that of the latter. This is particularly important for protecting joints and welds.

The behaviour of clad duralumin in sea water has recently been studied by P. Brenner* using the D.V.L. accelerated immersion test.† His results show that with only a 1 per cent. coating of pure aluminium the material will withstand immersion for at least two years in North Sea water without undergoing any deterioration in mechanical properties, provided that no annealing is carried out on the finished sheet. With a 5 per cent. coating of pure aluminium, the material may safely be annealed at 500 deg. Cent. for forty minutes, although so much copper diffuses into the surface layer in this time that the tensile strength of the sheet is increased by 2 kilos. per square millimetre. After one hour at 500 deg. Cent. the copper has diffused right through to the surface and the resistance to corrosion is therefore considerably reduced.

With B.S.S.-clad Duralumin diffusion of copper into the surface layers is remarkably slow; with a 5 per cent. cladding the copper of the core has penetrated only about half-way through the protective layer after three hours at 500 deg. Cent., and the corrosion resistance of the material is therefore scarcely affected. Artificial ageing at 140 deg. Cent. for twenty-four hours results in a 10 per cent., and at 175 deg. Cent. for twenty-four hours in a 30 per cent. reduction in the tensile strength of pure aluminium-clad sheet (6 per cent. cladding) after twenty-eight days in the D.V.L. test, whereas similar tests on B.S.S.-clad sheet show that the tensile properties are unaffected by either of these treatments. A still more marked difference between the two claddings is observed when the sheet is tested in a stressed condition, *e.g.*, after bending, in 3 per cent. salt solution containing 1 per cent. of hydrochloric acid; failure occurs in ten days with aluminium-clad sheet and in fourteen days with B.S.S.-clad sheet. The bad effect of copper in the coating shows up very clearly in this test. A specimen clad with aluminium containing 2 per cent. of copper failed in three days.

To sum up, it may be said that duralumin, even in the heat-hardened state, may be for all practical purposes rendered immune to salt water corrosion by a rolled-on coating of an alloy of pure aluminium with 7 to 9 per cent. of magnesium. Such coated material may be given any reasonable heat treatment without reducing its resistance to corrosion, the strength of the material is very little less than that of the core after any heat treatment, and the surface hardness is sufficient to ensure good wearing properties.

Veining and the Mosaic Structure in Metals.

By L. NORTHCOTT, Ph.D., M.Sc., F.I.C.

No. II. (*continued from October issue*).

CONNECTION BETWEEN VEINING AND MOSAIC STRUCTURE.

IT is suggested that the results described in the recent papers upon veining [1, 2] may be taken as further evidence as to the existence of a mosaic structure of the Darwin type in metals. As mentioned in the first part of this paper, it has been shown that veining is due to the precipitation of a constituent, usually oxide, from solid solution on cooling under such conditions that a pronounced network structure is developed. The irregular discontinuities on which the Darwin mosaic is based provide a simple explanation of why the deposit occurs in such a form. If the discontinuities inside the crystal are considered as miniature grain boundaries in which the difference in orientation between neighbouring "blocks" is very small indeed, the precipitation of minute quantities of material preferentially along such "sub-boundaries" is analogous to the preferential precipitation of much greater quantities of a second phase along the crystal boundaries which characterises the majority of two-phase alloys in which one phase predominates. In the latter case, the presence of the constituent in a network form along the crystal boundaries is the result of pre-existing differences in lattice orientation between neighbouring crystals. The presence of a second constituent in this form is sometimes of help in determining crystal size, since the boundaries are much more easily "developed" by the etching reagent, and is also responsible for the phenomenon of intercrystalline corrosion, *e.g.*, weld decay, experienced with certain alloys. Similarly, the presence of veining indicates that there are, within the crystal, pre-existing differences in orientation which, although far too small to be shown up by etching, have the effect of locating the initial precipitation of a constituent when this occurs only in a very small quantity. In the absence of such a constituent it is considered to be quite impossible with the present technique for the microscopical examination of metals to detect the presence of such small orientation differences as are responsible for the mosaic structure. The position of the major inequalities in orientation within the crystal may, however, be determined by the position of the deposits concentrated in them, in the same way that a crystal boundary deposit facilitates the location of the crystal boundary. It is considered that this is the part played by the veining constituent. The absence of veining is purely negative evidence, and does not indicate the absence of the mosaic structure, whereas the presence of veining gives positive indication as to the quantity or type of the major irregularities in the crystal structure. Reference has been made to the major irregularities, since it is probable that the differences in orientation of the different mosaic blocks are not all the same, and it is to be expected that the initial precipitation will take place where the orientation difference is greatest, other things being equal. This last qualification is necessary, since the initial precipitation is also governed by the degree of super-saturation and consequently the local concentration of the solute, which, as has recently been shown,[2] is not necessarily the same throughout the crystal, but may be affected by the dendritic structure. Now, it is a common occurrence for material to be deposited upon that already precipitated, and it is probable therefore that although it indicates the presence of the mosaic structure, the veining gives only an incomplete picture of that structure. On the other hand, from the X-ray reflection evidence, it is known that a crystal is rarely, if ever, a perfect mosaic, but assumes some intermediate form, so that the veining network will not approach perfection. For what might be termed ideal veining, it would be necessary to have a combination of perfect mosaic structure, together with complete and regular pre-

* *Z. Metallkunde*, 1936, 28, 276.
† *Ibid.*, 1932, 24, 57.

cipitation of the veining constituent on that mosaic, conditions unlikely to be fulfilled in practice.

In most instances the veining network is considerably larger than the mosaic proposed by Darwin in which the lower limit of size is of the order of 5000 Å.U., and this is to be expected, for the reasons given above, but there are examples where the veining network approaches this small value, as, for example, in the beryllium copper alloy shown in Figs. 1 and 2. In addition to this it must be remembered that, as pointed out by James, the mosaic passes gradually into the perfect crystal by the increase in size of the perfect

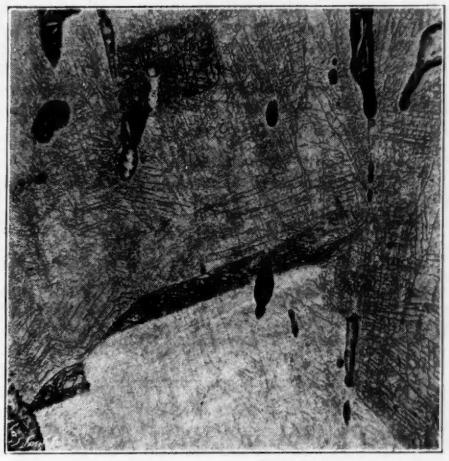


FIG. 1—*Beryllium-Copper Alloy Air-Cooled from 820 deg. Cent.* × *100.*

regions until one of them occupies the whole crystal, which may then be looked upon as an ideal crystal.

The two structures are similar in other ways. James[5] has discussed the artificial alteration of the state of perfection of crystals and cites an experiment upon rock salt,[18] in which this material showed appreciably less evidence of a mosaic structure after several hours heating at 590 deg. Cent., but more when it had cooled again to room temperature, and in this last condition it was only slightly less mosaic-like than originally. The differences were explained by a more perfect crystallisation or an annealing effect under the heat treatment. A somewhat similar effect was found in the work upon veining when the veining in slowly cooled copper was compared with that in the same specimen after quenching and tempering. In the latter case the veining was much more complete, more regular and the network much smaller than in the slowly cooled sample and suggested the presence of a more perfect mosaic structure. Also, in the copper-silicon and other alloys which had been annealed at high temperatures for a long time and very slowly cooled, the dimensions of the network were on a much larger scale than before the treatment, and the effect may be considered as being analogous to that found by James in rock salt. Conversely, air-cooled samples of different alloys showed veining which was finer and more complete than in samples very slowly cooled.

There are two other phenomena which may be included here in support of the mosaic theory, although until a more detailed examination has been made they are put forward only tentatively. It has been shown that in a cold-worked specimen annealed at a temperature in the neighbourhood of 500 deg. Cent. there was far less evidence of veining in the recrystallised areas than in those which had not recrystallised. Since the recrystallised material would have a different system of mosaic structure there would be less reason for the veining constituent to be retained in a network form, and more reason for it to coalesce into isolated particles as actually occurred. In the same series of specimens it was observed that twinning planes appeared to spread from the position where the veining touched the new crystals. Very slight irregularities in the lattice would assist in bringing about twinning at this point.

No evidence has been found to indicate the orientation differences of the different mosaic blocks in any one crystal. That the network structure is not revealed without the assistance of a second phase and that slip lines for the most part appear to be unaffected by veining indicate that the orientation differences must be extremely small.

It has often been suggested that the estimated strength of crystals is far greater than the strength

FIG. 2—*Beryllium-Copper Alloy Air-Cooled from 800 deg. to 500 deg. and Quenched.* × *2500.*

found by experiment, but many recent workers have pointed out the difference between the properties actually measured during the testing of a metal which deforms by slip and those of a non-ductile body in which the forces required to separate the atoms may be calculated. It may, however, be pointed out that whereas many writers have suggested the need of a mosaic structure to explain these alleged differences in crystal strength, no such suggestion is made now. On the contrary, it is evident that the mechanical effect of a mosaic of the type under consideration is likely to be small and may be expected to operate in the direction of increasing the hardness and strength and reducing the plasticity or ductility, at least at atmospheric temperatures. Although the blocks of the ideal mosaic show some lattice distortion at their boundaries, this will not be sufficient to be classified as actual cracks or pores. The effect may be considered as being similar to, but on a considerably smaller scale than, that exercised by crystal

boundaries which are known to bring about enhanced strength in metals and alloys. Slight increases in hardness due to the network form have in fact been observed.[3] Since the mechanical properties of recrystallised metals are similar to those of the materials before recrystallisation, it would be expected that the mosaic should occur in one as well as in the other, and this has been shown to be so with veining structures.

Some confirmation of the views expressed here is offered by the work of K. H. Moore,[21] who studied the structure of an age-hardened copper-beryllium (2·5 per cent. Be) alloy by means of a polarisation microscope in an effort to connect the favoured planes upon which the first precipitation takes place with the hypothetical net of planes making up the secondary structure of crystals. By means of crossed nicols, nets of lines were revealed indicating the surface traces of favoured planes, but they were invisible under normal or conical non-polarised illumination and it was undecided whether they were due to internal strain or to the actual presence of a precipitate. The spacing of two rectangular nets was measured as slightly less than 10,000 Å.U., indicating a possible connection between the planes favoured in precipitation and the secondary net of planes whose spacing has been estimated as being of that order of magnitude in metals. It was thought to be significant that among a series of samples aged for various times at the optimum temperature the first reasonably complete and measurable nets were found in the sample aged for the time found by other investigators to be the optimum time of treatment for producing hardness in this alloy. The veining developed in beryllium-copper,[2] however, was associated with only moderate hardness values and it is probable that this difference may be due to the veining network being less completely developed and consisting of coarser deposits as a result of the different heat treatment given.

An inquiry into the cause of the mosaic structure cannot, at this stage, be free from speculation, but mechanical strain during growth, or additionally in the case of metal crystals, during solidification and subsequent cooling, may possibly be the responsible factor, and it may not be necessary to consider, as Zwicky has done, the ionic structure of the crystal lattice. The development of internal strain is a feature which frequently manifests itself in metals, but further work is required before it can be stated whether the mosaic is associated with elastic or plastic strain. The influence of strain is shown by the tendency for a slight excess of veining to appear in quenched and tempered specimens at the junctions of three or more crystals and also by the difference in dimensions of the structures in the slowly cooled and in the quenched and tempered or air-cooled alloys. This artificial variation in the structure, not accompanied by much change in the mechanical properties, does not lend support to the theory requiring a mosaic structure for purposes of explaining differences in the properties of crystals. Nor is this theory substantiated by the experiments on rock salt by Joffé and Lewitsky,[19] who found that when the conditions of the experiment were so arranged that the presence of surface cracks was not effective in causing premature breakdown the measured tensile strength was only slightly less than that required by theory, nor by the existence of some crystals, for example, certain types of diamond, which approach very closely to the ideally perfect crystal, yet whose mechanical properties have not been found to be different from those of other crystals shown to have a pronounced mosaic structure.[20] Evidence of a mosaic structure in some diamonds was also found by optical methods using polarised light and the dimensions of the mosaic were of the orders found in the work on veining.

SUMMARY AND CONCLUSIONS.

The different theories of mosaic structures in metals have been very briefly reviewed. Attention has been drawn to recent investigations upon veining and sub-boundary structures in metals and to the similarity between the networks of these structures with the sub-crystalline irregularities postulated by the Darwin type of mosaic. Although complete confirmation of the association between the veining network and the pre-existing mosaic structures will be a matter of some difficulty, their dimensions and the similarity in the effects of heat treatment upon the two structures suggests some connection between them and further work on the subject is proposed.

REFERENCES.

[1] L. Northcott, *Journal* of the Iron and Steel Institute, 1932, ii, 267.
[2] L. Northcott, *Journal*, Institute of Metals, 1936, 59 (July).
[18] R. W. James, *Philosophical Magazine*, 1925, Vol. 49, page 585.
[19] A. Joffé and M. Lewitsky, *Zeitschrift für Physik*, 1926, Vol. 35, page 442.
[20] Sir R. Robertson, J. J. Fox, and A. E. Martin, "Philosophical Transactions" of the Royal Society, 1933–34, Vol. 232, page 463.
[21] K. H. Moore, *Physical Review*, 1934, Vol. 45, page 296.

The Phosphate Rust-Proofing Process.

SINCE its introduction thirty years ago the phosphate process for treating steel surfaces to provide a rust-resisting finish has found an increasing number of applications by virtue of steady improvements in efficiency. A survey of the present position, on which the following brief review is based, is provided by a recent collection of papers by American, German, Italian, and Russian workers dealing with various aspects of the process.[1]

HISTORICAL.[2]

The process depends on the property of certain acid phosphate solutions of forming an insoluble protective film on steel, but it was early recognised that the range of conditions for getting the best results was rather narrow. In Coslett's original process, worked out in Birmingham in 1906, weak phosphoric acid containing iron or zinc salts was used. Owing to difficulties in controlling the composition of the solution in operation the results were variable, and, at the best, the coating was not very rust-resistant unless oiled or painted. Coslett contended that the phosphate coating would prove advantageous as a foundation for paints by promoting adhesion and preventing spreading of rust from weak points, and this has been well borne out by experience. In order that the potentialities of the phosphate process should be realised it was necessary that the properties of the coating should be well established and a satisfactory solution be devised capable of easy control in operation. Richards, working in Coventry in 1911, had shown advantages for the use of an acid manganese phosphate solution, and later, about 1916, his patents, together with those of others, were taken over by the

Parkers in America and developed into the Parkerising process.

PRODUCTION OF PHOSPHATE COATINGS.

The Parkerising Process.[3]—The Parkerising bath consists of a solution in water, about 3 per cent. strength, of "Parker powder," which is essentially manganese dihydrogen phosphate together with some iron dihydrogen phosphate. The solution is contained in an iron tank and is kept heated practically to the boiling point by steam coils. The steel articles to be treated, free from scale and oily matter, are immersed in the solution; large articles may be suspended by hooks, whilst small parts may be contained in wire baskets or, preferably, in perforated rotating drums. At first, evolution of hydrogen gas occurs from the surfaces, but after a while this practically ceases, the parts becoming covered with a thin greyish-coloured coating. Treatment is usually complete in about an hour. The process may be considered as interaction between the outer surface layer of the steel with the dihydrogen phosphates in solution yielding an adherent layer of the mono-hydrogen phosphates of iron and manganese together with some neutral phosphate; this can be symbolised, with the omission of the manganese phosphate, thus :—

$$Fe + Fe(H_2PO_4)_2 = 2\,FeHPO_4 + H_2.$$
$$2\,FeHPO_4 + Fe = Fe_3(PO_4)_2 + H_2.$$

The bath is maintained by the addition of more Parker powder as required, according to an analytical test consisting in titration of a sample with standard alkali solution.

Practice appears to be closely similar in different countries. Large plants exist in this country and in America. In Germany the Parker process is taken over by the Metallgesellschaft A.G., of Frankfurt.

The parts are finished after phosphate treatment in a variety of ways depending on requirements, *e.g.*, with the aid of oils, lacquers, or enamel coatings. It is to be noted that unless coated with an opaque material it is usual to render the greyish phosphate coating black by means of a dye applied as a solution in water or oil. Oiling is preferably followed by centrifuging to remove excess.

The Atrament Process.[4]—This process, which is closely similar to the Parker process, is that of the I.G. Farbenindustrie A.G., of Frankfurt; a point of difference is that instead of powder the acid manganese phosphate is supplied in the form of a concentrated solution, 120 grammes of which will treat about 1 square metre of steel surface.

Rapid Processes.[3]—In the Parker Company's Bonderising process a phosphate bath is used containing a copper salt as accelerator, the treatment requiring only a few minutes instead of about one hour. No very great corrosion resistance is claimed for the coating, but as it provides a good bond for cellulose and similar finishes it has been widely adopted in the motor car industry. A rapid modified Atrament process is available.[4] This has the advantage of working at a lower temperature (55 to 60 deg. Cent.), and the consumption of added phosphate solution is less than in the regular process. The American Chemical Paint Company, in the Granodine No. 30 process, employs a zinc phosphate bath and applies alternating current to the parts under treatment; this process is a development of one of Coslett's early methods. In the Ford works, motor car lamps which are to be subsequently enamelled are treated by a similar electrolytic method, the period of treatment being 4½ minutes at 65 deg. Cent. The Parcolite process avoids the necessity of immersing the articles in a tank; a viscous phosphate preparation is applied to the surface by spraying and the layer is dried in an oven at 107 to 177 deg. Cent. Here again advantages are claimed chiefly for superior adhesion of organic finishes.

The Phosphate Process in Russia.—Tests have been carried out with phosphate powders available in Russia.[5] Two powders, viz., "Digophat" (from the Chemischen Fabrik, of Dsershinsk) and "Zim" (from the Zentralen Metallforschungsinstitut, of Leningrad) were found to be closely similar in chemical composition to Parker powder (P_2O_5, 49·2 per cent.; Mn, 14·6 per cent.; Fe, 2·7 per cent.) and gave phosphate coatings on steel showing little difference in protective power from those formed with the aid of Parker powder. The composition of the resulting coatings approximated closely to that of $MnHPO_4 . 3\,H_2O$ with small amounts of $FeHPO_4 . 3\,H_2O$. Difficulties in securing good coatings with another product, attributed to a rather high content of fluoride and sulphate as impurities, were overcome by the addition of calcium oxide and barium carbonate.

PROPERTIES OF PHOSPHATE COATINGS.

Whilst the phosphate coating is generally employed as a base for organic coatings, the protective properties of the phosphate coating itself, produced by a process such as Parkerising, have been extensively studied, as defects are likely to reduce the overall protection obtained. Various methods of testing have been used at the Parker laboratory at Detroit,[6] viz., outdoor weathering, immersion in fresh and salt water, salt spray and damp atmosphere tests for protective properties, and controlled bending, scratch and impact tests for mechanical properties. The cleaning treatment given to the steel prior to phosphatising has an important effect on the coating produced. The best method for removal of scale, &c., is mechanical cleaning, such as sand or shot blasting or emery treatment. With correct phosphate treatment the coating is fine-grained and uniform, and has the advantage of readily forming in recessed parts of the surface. Pre-treatment of the steel by pickling, *e.g.*, in hot dilute sulphuric or phosphoric acids, has been found to result in irregular covering; the coating consisted of large grains and gave comparatively poor protection in immersion tests in fresh or salt water.[7 8] Among other factors liable to give defective phosphate coatings are the presence of traces of grease not removed from the surface of the steel in the initial cleaning, too low a working temperature or incorrect composition of the solution.[4 9] The phosphate treatment of some twenty-eight carbon and alloy steels has been investigated;[10] the steels contained 0·02 to 1·14 per cent. of carbon with up to a few units per cent. of silicon, manganese, nickel, chromium, or tungsten, or about 0·5 per cent. of molybdenum or vanadium; steels with 1·4 to 2·4 per cent. of copper were included. The copper appeared largely to stop the formation of the phosphate coating, whilst molybdenum and tungsten in the presence of chromium prevented the coating from being as complete as desired. The other steels gave coatings which, whilst of satisfactory appearance, nevertheless varied in protective properties; thus in a salt water test, treated nickel-chromium steel and silicon-tungsten steel, for example, developed rust in only about one-fifth of the time required for treated carbon steel. Variations in carbon content appeared to have little effect. The phosphate coating formed on mechanically smoothed carbon steel was appreciably

thinner than on the etched material (8 μ compared with 45 μ), but the corrosion resistance of the thinner coating was the best, probably by reason of superior continuity.

Practically no dimensional change nor effect on the mechanical properties of steel occurs on phosphate treatment ; embrittlement or adverse effect on fatigue resistance appears to be absent, and the process is thus applicable to rust-proofing of springs.[4 10] Magnetic properties remain unchanged.[3] The coating, when correctly formed, is highly adherent to the basis metal, but owing to lack of ductility breaks in the coating may occur when the base is deformed.[4] Thus the process is best applied as a finishing treatment after forming. The adhesion is, however, considered adequate to withstand a reasonable amount of rough usage, such as, for example, on threads on which nuts are screwed. The heat resistance of the bare phosphate coating is satisfactory up to about 300 deg. Cent.;[4 10] above this temperature the coating tends to develop cracks which reduce its protective power, but with a superimposed heat-resisting paint good results have been obtained on engine exhaust pipes.[4] The phosphate coating is a non-conductor of electricity. This property plays an important part in rust prevention by minimising electrochemical couple effects at the steel surface. On the other hand, the insulating film makes electric welding difficult, and prevents electro-deposited coatings from being applied. The above notes on properties apply to coatings formed by a process such as Parkerising. Rapid processes of the type of Bonderising yield a thinner coating with less intrinsic protective power.[3 4] It has been established that such coatings promote adhesion of enamels and that the protection by an enamel is considerably better when applied on a Bonderised surface than on plain steel,[6] but little further information is available in the papers reviewed.

REFERENCES.

[1] *Korrosion und Metallschutz*, 1936, 12, 197–226. [2] O. Macchia, 197–202. [3] R. Justh, 202–208. [4] G. Büttner, 208–211. [5] A. S. Riwkind and G. M. Badaljan, 223–224. [6] H. J. Lodeesen, 219–222. [7] E. I. Dyrmont and S. D. Goldenberg, 222. [8] K. M. Domnitsch and A. M. Dubrowskij, 223. [9] O. Macchia, 211–219. [10] I. W. Gutman, 222–223, 225–226. (A comprehensive bibliography on the phosphate processes is given with the text of the above-mentioned papers.)

Hardness Testing.

THE most frequently applied test for control of the quality of metallurgical products is the hardness test. It is rapidly carried out, it does not involve much preparation of the material, it is usually a non-destructive test, and it affords a very considerable amount of information about tensile properties, uniformity, and success of heat treatment.

A wide variety of new forms of equipment for hardness testing is described and illustrated in an article on "New Hardness Testing Appliances," by W. Hengemühle.* Different improvements in presses for making Brinell tests, modifications of the Rockwell apparatus, including the Testor and Briro machines, and various forms of equipment for carrying out the Vickers diamond hardness test, such as the Briviskop and Dia-Testor, are dealt with as well as the Firth Hardometer and the Shore Monotron, which differs in principle from the others, in that it measures the load required to make an arbitrary impression, 0·045 mm. deep (0·36 mm. diameter). From the last two examples it will be judged that the machines described are not always to be classed as new. This applies also to several forms of dynamic hardness testing machines, based on the principle of the Scleroscope, which are included ; for example, the Sclerograph, the falling rod of which is tipped by a 5 mm. diameter steel ball, and the Duroskop, the readings of which are given by a rebounding pendulum hammer. Not only are the various machines described in detail, but special attention is given to the means of support of specimens of unusual form and size, requiring great width of base or testing height, and also, on the other hand, to methods applicable to the testing of thin sheets or of surface layers such as are produced by surface hardening, nitriding, &c. With application of the load for 30 sec. the number of impressions that can be made per hour is limited to about sixty, and consideration is given to speeding up the test. Curves are given to show how cutting down the time of application of the load to 5 sec. or even 1 sec. affects the results. The following values are read from the curves :—

Brinell hardness number. Load held 30 secs.	Percentage increase when load is held for 1 sec.	5 secs.
400	0·5	Nil
200	3·0	1·2
100	7·0	3·0

Though reduction of the 30 second loading may be

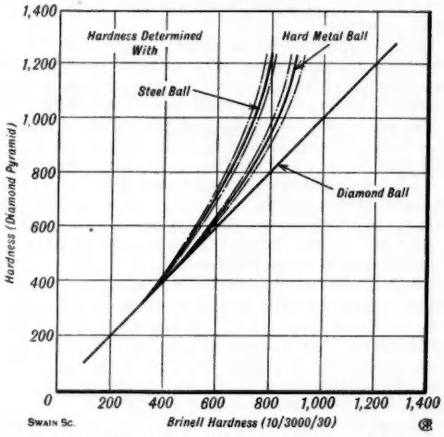


FIG. 1—*Relation Between Vickers and Brinell Hardness.*

permissible for hard materials, it is certainly undesirable for the softer grades of steel, and for metals of similar or lower hardness.

The Brinell-Vickers scale is rightly regarded by the author as the standard of reference. There is reason to believe that the Vickers diamond pyramid test and the Brinell test with a diamond ball would show exact agreement, though even the diamond hardness number will show departure from the ideal curve for the perfectly rigid ball or pyramid. The actual relationship between Vickers and Brinell hardness numbers, shown in Fig. 1, is dependent on the hardness of the Brinell ball. This has been recognised by the B.S. Specification No. 240, part 2, which specifies a minimum hardness for the ball. The curve for steel balls in Fig. 1 indicates exact agreement between Brinell and Vickers tests below 350, but more general experience seems to be that the

* *Stahl und Eisen*, Sept. 10th, 1936, 56, 1017.

Brinell number is from 2 to 5 per cent. lower than the Vickers number within this range of hardness. The relation between Rockwell and Brinell hardness numbers has been the subject of a large number of investigations, which are summarised in Fig. 2, the limits shown by the double lines representing the scatter of the experimental results. A certain amount of scatter, especially at high hardness, is to be expected from the nature of the tests, but on the whole the results of comparison by different investigators show very good agreement.

Of all hardness tests the one most widely studied has been the Brinell test. The able summary of the principles underlying this test in Dr. H. O'Neill's book, "The Hardness of Metals and its Measurement," published two years ago, not only revealed

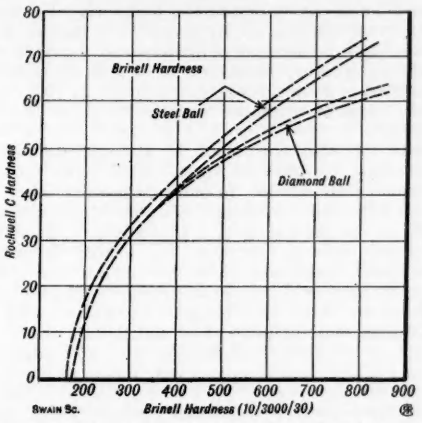


FIG. 2—*Relation Between Rockwell C and Brinell Hardness.*

the extent of the literature on this subject, but showed how the results of the test were linked up with other physical properties of the material, with the characteristics of the ball, and with the procedure adopted in testing. In the hope of making the test even more accurate and more significant than it now is in practice the United States National Bureau of Standards has carried out a complete review of the position, which has been published under the title "Determination of the Brinell Number of Metals," by S. N. Petrenko, W. Ramberg and B. Wilson.† Their endeavour has been, by the combination of existing knowledge supplemented by actual tests on thirty-seven different metals and alloys to account for and remove such discrepancies in the measurement of Brinell hardness as may be due to the apparatus and procedure, to non-uniformity of specimens, their curvature and thickness, to the spacing of indentations, inclination of load to the normal and finally to the ball, its dimensions, shape, and deformation under load.

It would appear, in view of the existence of Dr. O'Neill's book, which is not mentioned by the authors, that this work of the Bureau of Standards has involved considerable duplication of effort. The authors have, however, at least gone carefully over some of the same ground and have extended the available data by their own investigations. The work was carried out entirely on an ordinary "Alpha" press and the measurements of diameter were made with the ordinary Brinell microscope having an eye-piece scale of 7 mm. range, graduated in 0·1 mm. A very interesting part of the work is the discussion of the deformation of the ball under load, and the effect of this on hardness number. The tests are summarised in a diagram Fig. 3 which may be compared with Fig. 1. The actual hardness numbers obtained with steel, Carboloy (tungsten carbide), and diamond balls are compared with the calculated value for a perfectly rigid ball.

The authors' final recommendations as to the most suitable conditions of test refer to metals having a Brinell hardness number greater than 70. They also appear to refer throughout to tests with a ball of 10 mm. diameter. The following is their list of recommendations:—

(1) APPARATUS AND PROCEDURE.

(*a*) The loading mechanism should be operated to give a uniform rate of loading not exceeding 500 kilos. per second.

(*b*) The maximum load should be applied for 30 sec.

(*c*) The error in the load applied by the machine should not exceed ½ per cent. This should be checked by periodic calibration with a proving ring or other suitable device.

(*d*) The calibration of the apparatus used for measuring the diameter of the indentation should be

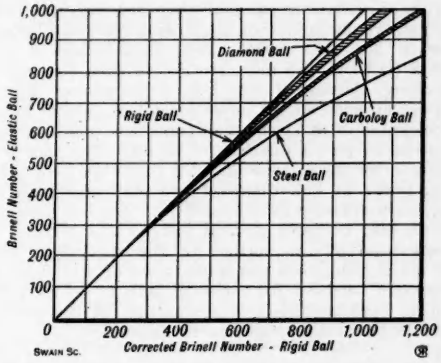


FIG. 3—*Brinell Hardness as Determined with Steel, Carboloy and Diamond Ball, Compared with Corrected Value for a Perfectly Rigid Ball.*

checked frequently. The maximum error in the reading at any point on the scale should not exceed 0·01 mm. The indentation diameter should be read in two or more mutually perpendicular directions.

(2) SPECIMEN.

(*a*) The Brinell number should be computed from the average of diameter readings in at least four equally spaced directions if the indentation has a non-circular boundary. Care should be taken to polish the surface of the specimen to such a finish that the error in diameter reading due to tool marks does not exceed 0·01 mm.

(*b*) If the indentation is made on a curved specimen the minimum radius of curvature of the specimen should not be less than 25 mm. for a 10 mm. ball. The diameter of indentation should be taken as the average of the two principal diameters.

(*c*) The specimen should be at least 0·4in. thick.

(*d*) The distance of the centre of the indentation from the edge of the specimen should be at least three times the diameter of the indentation.

† U.S. Bureau of Standards *Journal of Research*, July, 1936, p. 59.

(*e*) The distance between centres of adjacent indentations should be at least three times the diameter of the indentation.

(*f*) The angle between the load line and the normal to the specimen should not exceed 2 deg.

(3) INDENTING BALL.

(*a*) A difference between the average diameter and the nominal (10 mm.) diameter of the ball should not exceed 0·025 mm. (0·001in.). The average diameter should be the average of six or more different diameters of the ball.

(*b*) The difference between any individual diameter and the average diameter of new balls should not exceed 0·025 mm. (0·001in.).

(*c*) The material of the indenting ball (*e.g.*, steel, Carboloy, diamond) must be specified in quoting Brinell numbers greater than 500. The permanent compression of the loaded diameter of the ball after any indentation on a specimen having a Brinell number less than 500 should not exceed 0·01 mm. If, however, steel balls are used on specimens having Brinell numbers greater than 500, the permanent compression after any indentation should not exceed 0·025 mm.

The use of Carboloy balls is recommended for indentations on any specimen having a Brinell number greater than 500.

It is of interest to compare these recommendations with the requirements of the British Standard Specification No. 240—1926. Recommendations 1 (*d*) and 2 (*c*) to (*e*) are more restrictive than the corresponding clauses of the B.S. Specification which require an accuracy of measurement of ±0·05 mm., a thickness of at least seven times the depth of the impression, and a distance of at least 2½ times the diameter of the impression. On the other hand, the B.S. limits of ball diameter are only one-tenth of that recommended in 3 (*a*) and (*b*). The B.S. Specification also contains general instructions about the preparation of the surface of the specimens, but though it recognises the importance of specifying a minimum hardness for the steel balls to be used for testing hard materials, a recognition of the use of hard carbide balls would now be desirable.

Free-Cutting Aluminium Alloys.

THE use of free-cutting aluminium alloys—that is, alloys which can be machined with the minimum of attention and best results in automatic lathes—is a natural consequence of the extended use of aluminium throughout the world. In Germany, in particular, the increasing use of aluminium has received an added impetus from the restrictions imposed upon the use of copper-base alloys, and this is reflected in the increased amount of research devoted to the investigation of the production and properties of free-cutting aluminium alloys.

Thus, E. Vaders[1] has summarised some of the characteristics which an alloy should possess if it is to be regarded as "free cutting." Upon machining, such an alloy should give turnings which are short and brittle, as opposed to the long spirals given by ordinary alloys. Further, the surface left after machining should be smooth and regular, and not pitted by the breaking out of inclusions. It must be understood that the conditions under which an alloy should show the above characteristics are those obtaining in automatic machining operations such as have been developed for the treatment of free-cutting brasses, and this means that the effect of variation of rates of cutting and feed and other allied factors must be ignored temporarily, although they have a profound effect.

The essential features of the structure of a free-cutting alloy are that it shall consist of a matrix with embedded particles which may be either softer or harder than the matrix. An alloy with a uniformly hard structure may give a good finish because of intrinsic brittleness of its chip, but a structure consisting of hard particles embedded in a soft matrix may be free cutting as regards shortness of chips, while the surface finish is poor. This is due to crushing and breaking out of the hard and brittle constituent, and silicon-aluminium alloys afford a good example of this type of structure. For best results, both as regards shortness of the turnings and resultant finish, a structure consisting of a soft constituent embedded in a harder matrix is of most use, and this is the type of structure possessed by the leaded brasses.

Lead has also been used in attempts to confer free-cutting properties upon aluminium alloys, together with similar insoluble elements such as bismuth, cadmium, and thallium. The chief difficulty to be met is the segregation which is a result of the difference existing between the specific gravities of lead and aluminium, and G. Masing and G. Ritzau[2] have endeavoured to devise means whereby this segregation may be limited. Working with a duralumin type of alloy they added lead either by means of reducible lead salts or by lead-containing temper alloys, and produced cast billets of approximately 1in. diameter by 3½in. long. A billet solidified after one minute's treatment with sufficient lead chloride to add 2 per cent. of lead to the alloy was found to contain 1·6 and 1·9 per cent. of lead in the upper and lower regions respectively. In another melt treated with the same amount of lead chloride but for ten minutes, the contents in the upper and lower regions had become 1·3 and 2·6 per cent. respectively, and further attempts to introduce 4 per cent. of lead into a melt resulted in a difference in lead content of 4·06 per cent. between top and bottom. These results, considered in relation with the experimental difficulties encountered in the use of volatile chlorides, must be regarded as unsatisfactory.

Of the temper alloys used, one containing lead 25, nickel 12·5, and copper 62·5 per cent. gave the most promising results, since one minute's treatment with sufficient temper alloy to produce 2 per cent. of lead in the billet gave 1·3 and 1·4 per cent. of lead in the upper and lower portions respectively. A ten-minute treatment with the same amount of temper alloy showed 1·2 and 1·3 per cent. of lead in the two positions. Other temper alloys which were used, but which did not give such promising results, included copper 50, nickel 10, lead 40 per cent.; magnesium 35, lead 65 per cent.; copper 55·5, lead 44·5 per cent.; and copper 70, lead 30 per cent.

Masing and Ritzau also attempted to reduce segregation by applying soundwaves to a melt containing lead by means of a rod vibrated by an electric horn. The rod was dipped into the melt and ten minutes' treatment was applied. The resulting billets showed some variation in lead content, for example, from 0·5 to 1·0 per cent. in a billet containing 1 per cent. lead, while another of 4 per cent. lead varied from

1·72 up to 10·96 per cent. This is unsatisfactory and it may well be that agitation has had the effect opposite to that desired—that is, coalescence of the lead droplets may have taken place.

Since the above work has been carried out upon free-cutting alloys which have a soft constituent as a free-cutting agent, it is interesting to compare the work of H. Bohner,[3] who has investigated the effect of hard, brittle aluminides in the same capacity. This author has carried out experiments upon alloys of the Hydronalium type, and has noted the different modes of distribution of Al_3Mg_2 in the alloy. In cast billets it occurs in a coarsely precipitated form, but after working and heat treatment the constituent is precipitated more finely either at grain boundaries or within the grain or both. This in itself causes a difference in machining properties, but it was also found that the addition of elements which will form intermetallic compounds with aluminium causes the machining chips to be shorter in length. The elements quoted by Bohner are manganese, iron, chromium, vanadium, titanium, and molybdenum. With any one element, an appreciable percentage may cause dendrites of some size to form, and these are dangerous since they may tear out of the matrix upon machining or become crushed and lead to difficulties in deformation processes due to their natural hardness and brittleness. With more than one of the above elements, although the total percentage is maintained at about the same figure, the size of the primary compound crystals decreases while their number may increase.

This in itself is an important step, but Bohner has also shown that heat treatment can be usefully applied with the object of breaking up the primary crystals of the aluminides produced by the above process. The explanation offered is that magnesium absorption occurs, and it is stated that Hydronalium DBA has been evolved with a view to its use as a free-machining alloy in the light of the above discoveries. It is stated that the physical properties of the alloy are about normal except that the elongation is a little lower. The nature of the chips obtained upon machining is dependent upon the magnesium content of the alloy, the degree of deformation, the heat treatment, and the nature and quantity of the additional elements and their reactions under treatment.

It appears, therefore, that there are two methods available for the improvement of the machining properties of aluminium alloys. Both of these methods involve the use of additions, the first the use of inclusions of soft, insoluble lead (or similar elements), and the second the use of inclusions of hard and brittle intermetallic compounds.

The disadvantages attached to the use of lead are, first, its liability to segregation; secondly, that hot working is restricted to temperatures below the melting point of lead, and finally, that mechanical properties and corrosion resistance are impaired. The use of hard intermetallic compounds may lead to difficulties in working, and the surface finish may be poor owing to tearing out of the brittle material, but this should only occur if the size of the particles is allowed to become too large.

In both cases it must be admitted that the size of particles of the free-cutting agent is a most important factor, and while heat treatment and increase of the number of added elements may solve the problem in the case of the intermetallic compounds, the problem of the best method of dispersion of the soft, heavy constituent has yet to be completely solved. An attempt to form an almost colloidal suspension would seem to be worth while, but information is also required upon the relative effects of lead dispersed throughout an alloy in particles of different sizes. It can be visualised that an exceedingly fine suspension will have little effect compared with a lesser number of particles of somewhat larger diameter, while a few particles of gross dimensions will have erratic effects and will favour segregation.

References.

[1] E. Vaders, *Metallwirtschaft*, 1936, 15, 814.
[2] G. Masing and G. Ritzau, *Z.Metallkunde*, 1936, 28, 293.
[3] H. Bohner, *Z. Metallkunde*, 1936, 28, 290.

Books and Publications.

Das Technische Eisen, by Paul Oberhoffer. Third edition, revised and enlarged by W. Eilender and H. Esser. 9¾in. by 6½in., pp. x+642. Berlin: Julius Springer. 1936. RM. 57.

In its second edition (1925) this book made a strong appeal to metallurgists of all nationalities on account of the well-balanced and scientific treatment of the physical and technological properties of commercial iron and steel. Unfortunately, the author's career of fine achievement and great promise was cut short by his early death in 1927. The revision of the book has been undertaken by Professors Eilender and Esser.

In general arrangement the book remains the same, the principal divisions relating to the constitution of the binary and ternary alloys of iron and carbon, the influence of temperature on the properties of steel, the effect of mechanical working and of heat treatment, and the properties of malleable, grey and white cast iron. The small increase in the length of the text does not properly reflect the additions that have been made, since some parts of the original have been abbreviated, so gaining in conciseness, but losing nothing in value. For example, the chapters on cast iron have been reduced by twenty-one pages, but alloy cast irons and other recent developments receive full attention. Perhaps a better indication of the extension of subject matter is that the number of diagrams and illustrations has increased from 610 to 762.

The long chapter on the constitution of the iron alloys has been revised and extended, and on the whole may be considered as thoroughly up to date. There are, however, some exceptions. The diagram given for iron-manganese does not show the important modifications introduced by Dr. Gayler (1933), particularly the peritectic reaction at 65 to 74 per cent. of manganese, and its consequences in the solid at lower temperatures. In the iron-arsenic system the $\delta\ \gamma$ peritectic is indicated in accordance with Oberhoffer and Gallaschik's diagram, though there is some evidence, not yet fully confirmed, that arsenic forms a γ loop. The liquidus and solidus of the iron-chromium diagram given were rendered obsolete by the work of Adcock (1931), which is not mentioned. There is, however, some quite recent justification for retaining Wever and Jellinghaus's ε phase (FeCr). The ternary systems of carbon, iron and the special elements are also described, and in view of the fact that the recent monumental work of Hansen deals only with the binary systems, this is a welcome feature. It is an indication of the rate at which work

on ternary equilibrium diagrams is now proceeding, and not of any fault of the authors, that the discussion of some of these is already rendered out of date by subsequent publications, *e.g.*, that of the iron-manganese-carbon system by Vogel and Doring's, recently published study of the constitution of these alloys.* This fact makes it necessary, in some instances, to modify the authors' conclusions in the light of results which have appeared since, say, the middle of 1935.

Revision has been thorough in other directions also, and special mention may be made of the new section on flakes in steel, in which the hydrogen theory is given full weight, and of that on precipitation hardening, which is the best summary of this subject, as it applies to the alloys of iron, that has yet appeared in any book of reference. Here again, however, the progress of investigation is so rapid that the section must be read in the light of further work which has appeared during the last eighteen months. A new section on nitriding has been added to complete the revised account of methods of surface hardening.

The work is planned and the subject matter presented in a clear and logical manner. A portrait of Oberhoffer is a fitting frontispiece. The book is very well produced and illustrated, but many who would be glad to possess it may be deterred by its high price.

The Alloys of Iron and Carbon. Vol. I, *Constitution.* By SAMUEL EPSTEIN. 8vo, pp. xii+476. New York and London: McGraw-Hill Publishing Company, Ltd. 1936. 30s.

THIS book is one of the series of comprehensive critical summaries of existing knowledge of iron and its alloys, published under the auspices of the Iron Alloys Committee of the Engineering Foundation of America. Although in order of publication it is the sixth of the series, in logical sequence it would be the second, preceded only by the volume on "The Metal—Iron." The mass of published information on the plain carbon steels is so enormous that the author has been forced to make a selection. Even then it was impossible to compress into a single volume all the really important data about plain carbon steels which it was desired to record, and a second volume dealing with the properties which are not covered by the headings constitution and heat-treatment is promised in the near future. The author has made a carefully considered and unbiassed selection, and his judgment in this matter renders the "Author's Summary," which is a feature of nearly every chapter of each book of this series, of exceptional interest.

The contents include a discussion of the iron-carbon diagram, and of the iron-graphite diagram, arrested transformations, principles underlying heat-treatment, changes in tempering, the macrostructure and microstructure of iron and steel, effect of mass and of furnace atmosphere in heat-treatment, the operations of quenching, tempering and carburising, inhomogeneity and other factors, such as grain size, affecting the quality of commercial iron-carbon alloys.

The most important part of the volume is that dealing with the iron-carbon diagram, and the author's summary is here particularly valuable. Every point and line is examined in detail and an estimate is made of the probable error involved in fixing its position. Following this discussion, a list is given of the principal uncertainties which still require further investigation. In considering the application of thermodynamics to the iron-carbon diagram the author concludes that the data which form the basis of the thermodynamical calculations are not known with sufficient accuracy to be of appreciable aid in selecting the most probable location of the phase boundaries. Therefore no importance is attached to thermodynamic calculations in selecting the most probable values for the diagram; but, on the other hand, full weight is given to deductions from the experimentally determined diagram, based on thermodynamic considerations. For example, it is held that carbon exists in the melt as Fe_3C and that the carbon-austenite solubility line selected from the experimental determinations is consistent with the existence of carbon in austenite as Fe_3C, probably sufficiently dissociated to account for the rapid diffusion of carbon in iron in the austenitic range of temperature. The iron-graphite diagram is reviewed in a similar manner, and this leads in the later part of the book to some consideration of the constitution of cast iron, graphitisation, and the effect of superheating and of "hereditary tendencies," a vague term which has often been employed as a cloak for ignorance. The constitution of cast iron cannot be interpreted in terms of a binary diagram, and it may be recalled that it is discussed at greater length in the book on "The Alloys of Iron and Silicon" in this series. Nevertheless, although the pure iron-carbon alloys may have no immediate practical utility and although equilibrium may never be encountered in practice, the true equilibrium diagram is of primary importance not only on its own account as giving a record, the interpretation of which can be modified to suit the departure from ideal conditions met with in practice, but also as the only foundation on which an accurate understanding of the effects of alloying elements can be based.

Engineers, producers and users of steel may regard this part of the book as mainly useful for laboratory research workers, but even so, much remains which will be of direct interest to these classes of readers. The principles underlying hardening are of fundamental importance in practice. Such subjects as segregation, non-metallic inclusions and their effects, internal stresses in quenched steels, ageing and grain size control are dealt with in a thorough manner. Mass effect is discussed, though this subject, apart from principles, can only be treated satisfactorily in books on alloy steels. Attention is devoted to American investigations, some of which have already been reported, as, for example, the work on "shatter cracks" in rails, and others, such as the work on heat-treated wire arising out of the failure of the components of two large suspension bridges at Providence, R.I., and at Detroit, which are incomplete or of which no full and concise report is yet available.

The author is to be congratulated on the way in which he has carried through the first part of his task, and his supplementary volume on the "Properties" of the plain carbon steels will be awaited with interest.

* See THE METALLURGIST, February 28th, 1936, page 102.

END OF VOL. X.